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АННОТАЦИЯ

Исследовались при комнатной температуре ЯМР-параметры ядер ^{31}P в аморфных сплавах Ni-P, полученных 4-мя способами /химическим восстановлением из хлоридной и сульфатной ванны, электролизом и быстрым охлаждением из расплава/. Те параметры ЯМР, которые зависят от общих свойств электронной структуры, были одинаковыми во всех типах сплавов с одинаковым химическим составом. Вклад полезависящей ширины сигнала, чувствительный к флуктуациям электронной структуры, указывает на неоднородность электронной структуры во всех типах сплавов и на более высокую степень неоднородности в случае химически восстановленных сплавов, чем в сплавах, полученных другими способами.

KIVONAT

Szobahőmérsékleten vizsgáltuk a ^{31}P NMR paramétereket amorf Ni-P ötvözeteken, amelyeket négyféle módszerrel állitottunk elő /kémiai redukcióval kloridos és szulfátos fürdőből, elektrolizissel, olvadékból gyorshütéssel/. Azok az NMR paraméterek, amelyek az elektronszerkezet átlagos tulajdonságaitól függnek, azonosnak adódtak mindegyik tipusu ötvözet, ugyanolyan kémiai összetétel esetén. Az elektronszerkezet fluktuációira érzékeny térfüggő jelszélesség járulékból azt a következtetést lehetett levonni, hogy mindegyik tipusu ötvözetben inhomogén az elektronszerkezet és az inhomogenitás nagyobb a kloridos fürdőből kémiailag redukált ötvözetek esetén, mint a többi módszerrel kapott mintáknál.

^{31}P NMR PARAMETERS OF AMORPHOUS Ni-P ALLOYS PREPARED BY DIFFERENT METHODS

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ABSTRACT

Room temperature ^{31}P NMR parameters were studied on amorphous Ni-P alloys prepared by four methods (chemical reduction from chloridic and sulphuric bath, electrodeposition, melt quenching). Those of the NMR parameters which depend on the average properties of the electronic structure are the same for each kind of alloys with the same chemical composition. The field-dependent linewidth contribution which reflects the fluctuations in the electronic structure indicates that all the alloys have an inhomogeneous electronic structure and a higher degree of inhomogeneity is observed in samples prepared by chemical reduction from the chloridic bath in comparison with alloys obtained by the other methods.

INTRODUCTION

The Ni-P alloy system can be obtained in the amorphous state in a wide concentration range and it can be prepared by a variety of techniques: chemical reduction (CR) [1], electrodeposition (ED) [2], flash-evaporation [3], and melt quenching (MQ) [4]. Relatively few efforts have been devoted to a comparison of the properties of amorphous Ni-P alloys prepared by different methods. An X-ray study of Waseda et al. [4] has shown a good overall agreement in the structure of ED and MQ amorphous $Ni_{80}P_{20}$ alloys. According to the neutron diffraction, Compton scattering and X-ray photoemission spectroscopy study of Suzuki et al. [5] there are no significant differences of atomic and electronic structures between ED and MQ amorphous $Ni_{81}P_{19}$ alloys. On the other hand, Bennett et al. [6].

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reported a rather large difference between the Knight shifts of CR and ED amorphous Ni-P alloys in the 18 to 25 at.% P concentration range.

The subject of the present work was a detailed ^{31}P nuclear magnetic resonance (NMR) study of amorphous Ni-P alloys prepared by different methods, in order to see the influence of the chemical composition and the way of preparation on the stucture and electronic properties of this alloy system. In the present paper the experimental conditions and the results obtained are described and briefly discussed.

EXPERIMENTAL PROCEDURE

The samples were prepared by four different methods. Chemical reduction was performed from solutions containing either hydrocloric or sulphuric acid (referred to as bath C and bath S, respectively). The details of chemical reduction have been described elsewhere [7]. The electrodeposited alloys were prepared from a bath containing typically 0.57 mol/dm^3 $NiSO_4$, 0.19 mol/dm^3 $NiCl_2$, 0.24 mol/dm^3 basic $NiCO_3$, 0.5 mol/dm^3 H_3PO_4, 0.5 mol/dm^3 H_3PO_3. The pH-value was 0.5, the bath temperature 75^{o}C, the deposition current density 10 A/dm^2 and a 99.9 % purity Ni sheet was used as the anode. The melt quenched alloys were obtained by the Liebermann-Graham technique [8].

The ^{31}P NMR studies were performed on a home-built continuous wave (CW) spectrometer operated at 2.3, 4.3, and 6.6 kOe external magnetic field and on a Bruker SXP 4-100 pulse spectrometer with a maximum field of 21 kOe. The peak-to-peak distance δH of the CW absorption derivative signal was measured at room temperature as a function of the external magnetic field H. The Knight shift K was measured with respect to amorphous solid red phosphorus at room temperature. For the measurement of the spin-lattice relaxation time T_1 the pulse sequence $\pi-\tau-\pi/2-\tau_o-\pi$ was applied for temperatures ranging from 80 K to 300 K. Part of the experimental results on some of the ED samples has already been given [9,10].

The measured linewidth values (δH) were fitted by the formula [11]

$$(\delta H)^2 = (\delta H_o)^2 + (k_1 \cdot H)^2 \qquad (1)$$

where δH_o is the field-independent linewidth contribution and the parameter k_1 describes the strength of the field-dependence of the linewidth. As it was pointed out by Hasegawa et al. [11] the field-dependence of the ^{31}P NMR linewidth observed in non-magnetic amorphous alloys originates from a distribution of the Knight shifts which is a consequence of the inequivalency of the P atomic sites. Therefore, the parameter k_1 reflects the inhomogeneity of the electronic structure. We prefer the parameter k_1 rather than the parametrization introduced by Hasegawa et al [11]. The reason for this choice is that in our formulation k_1 is dimensionless and it can be directly identified as the width of the Knight shift distribution as it can be inferred from eq. (1).

RESULTS AND DISCUSSION

The obtained values of δH_o range from 1 Oe to 1.7 Oe and do not show any systematic change with either composition or preparation technique but are considerably higher than the direct dipolar broadening calculated using a DRPHS amorphous model cluster [12]. A more accurate method for the measurement of the P-P interaction [13] will possibly allow to determine more precisely the excess moment which is necessary for deducing any conclusions in this respect.

Figure 1 shows the Knight shift K and the parameter k_1 as a function of P content in amorphous Ni-P alloys. Both parameters decrease with increasing phosphorus concentration. Similar trends in K and k_1 were observed in MQ $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ metallic glasses ($16 \leq x \leq 26.5$) by Hines et al. [14,15] with slightly higher K values. The present Knight shift values agree with those of Bennett et al. [6] for CR samples, but disagree with their low and concentration independent K values for ED samples. This discrepancy is not understood at present. Our Knight shift values seem to extrapolate through the corresponding values of the crystalline Ni_3P and Ni_5P_2 compounds, indicating an overall similarity in the electronic structures of the amorphous alloys and their crystalline counterparts.

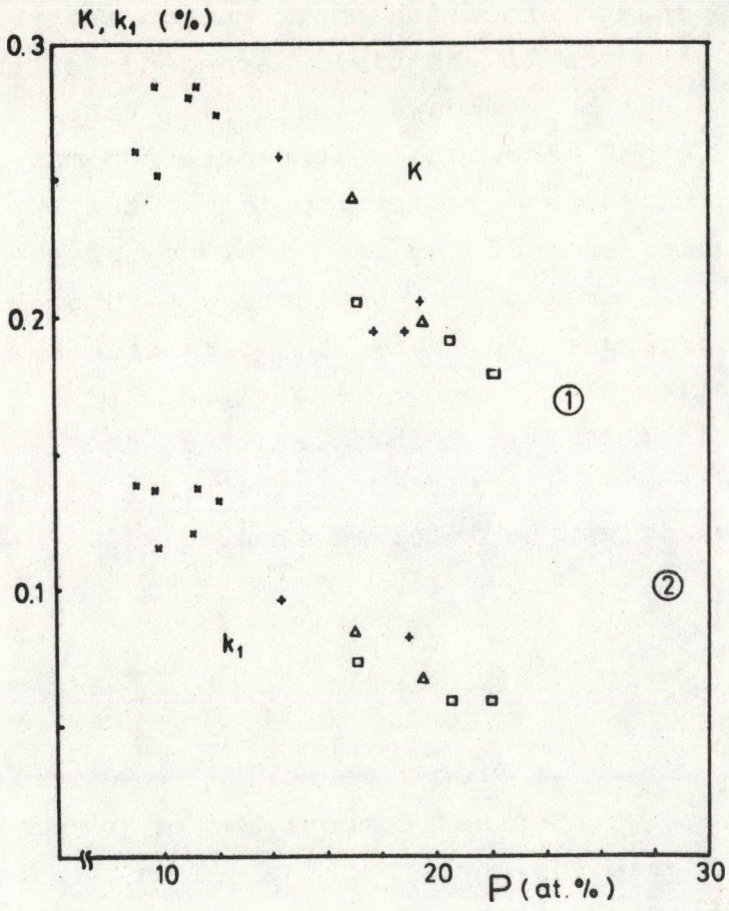

Fig. 1. Room temperature ^{31}P NMR Knight shift K /upper symbols/ and field-dependent linewidth parameter k_1 /lower symbols/ vs P content in amorphous Ni-P alloys prepared by chemical reduction from chloridic /×/ and sulphuric /+/ bath, electrodeposition /□/, and melt quenching /△/. (Symbols ① and ② refer to the Knight shift of the crystalline compounds Ni_3P and Ni_5P_2, respectively [6].)

Hines et al. [15] gave a detailed discussion which terms may give contributions to the ^{31}P NMR shift in non-magnetic amorphous alloys. Without going into the details, it is remarked here only that irrespective of the relative importance of the individual shift contributions, the Knight shift always consists of terms which contain the spatial electronic densities and the magnetic susceptibilities in the form of products. Keeping this in mind the Knight shift can simply be considered as a measure of the spatial average of these quantities and the Knight shift distribution measured by k_1 characterizes their spatial fluctuations. It is demonstrated by the lower part of Fig. 1 that amorphous Ni-P alloys have an inhomogeneous electronic structure and the inhomogeneity decreases with increasing P content.

In Fig. 2 the parameter k_1 is plotted against K with P content as an implicit variable. It can be seen that there is a correlation between k_1 and K. We define the degree of inhomogeneity in the electronic structure to be higher if k_1 is greater for the same value of the average Knight shift K. In this sense the ED and MQ Ni-P alloys seem to show a common behaviour while the CR samples, especially those deposited from bath C occur to be more inhomogeneous. Thus a k_1 vs K plot enables to distinguish between samples

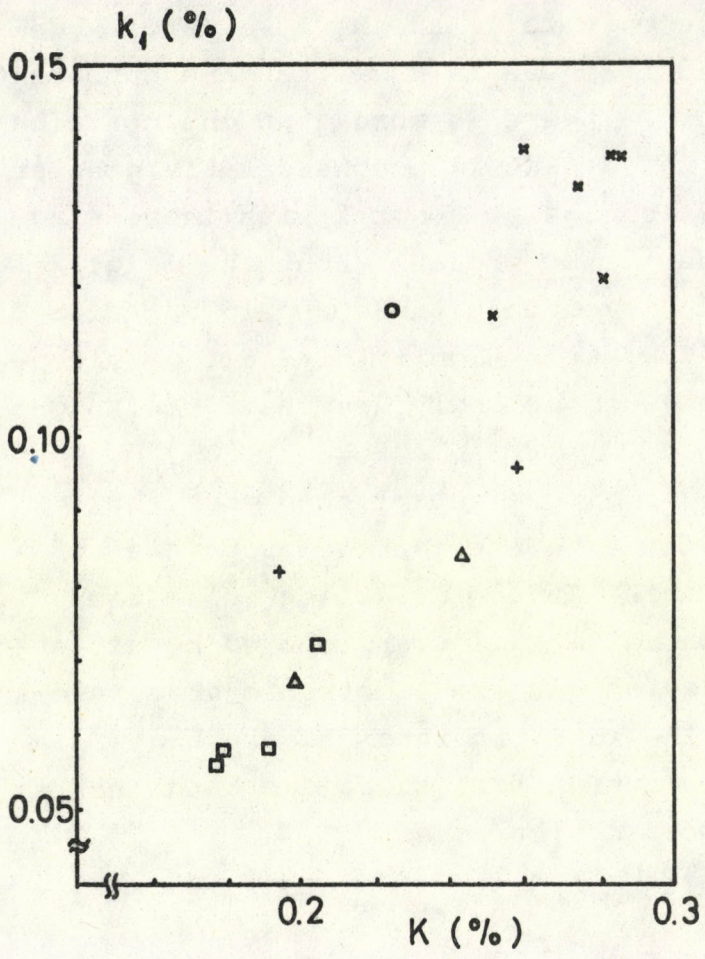

Fig. 2. Parameter k_1 vs the Knight shift K for amorphous Ni-P alloys. The same symbols are used as in Fig. 1. Data point o is taken from Ref. [6] /chemical reduction without bath specification/.

with different inhomogeneities in the electronic structure. Care must be taken, however, since a different degree of inhomogeneity may arise from either real differences in the alloy properties or from impurities inherently incorporated during the deposition process. Detailed transmission electron microscopy, differential scanning calorimetry, and transport property studies on the present samples [7] have also shown that, among the preparation techniques used here, chemical reduction from bath C results in the most inhomogeneous samples.

The spin-lattice relaxation time T_1 was measured for four samples between 80 K and 300 K and a T_1T = const. relation was found. This shows that the spin-lattice relaxation is of Korringa type, that is, it originates from the interactions with the conduction electrons in these alloys. The T_1T values obtained are: 1.01 K s for 14.3 at.% P (CR from bath S), and 1.11, 1.26, and 1.34 K·s for 17.1, 20.5, and 22 at.% P, respectively (ED samples). On the rest of the alloy samples, T_1 was measured at room temperature only. The room temprature spin-lattice relaxation rate T_1^{-1} for 36 MHz decreased from 380 to 240 s^{-1} between the lowest and highest P compositions given in Fig. 1.

Using the measured room temperature values of K and T_1, the Korringa ratio k was calculated for the amorphous Ni-P alloys. The Korringa ratio is defined by $k = K^2T_1T/S$, where $S = 1.605 \cdot 10^{-6}$ K·s for ^{31}P nuclei. A value k = 1 is expected if non-interacting con-

duction s-electrons contribute only to T_1 and K. A value of k deviating from unity is obtained if there is an exchange enhancement of the conduction electrons or if there is more than one contribution to T_1 and K [16]. It is found that k is considerably greater than unity and decreases from about 4 to about 2 with increasing P content. We don't want to decide at present about the origin of the high k value, but it is believed that there should be a considerable d-polarization shift contribution in Ni-P alloys since introducing Cu into the Ni-P system strongly decreases the Knight shift [17].

Summarizing the results, it can be established that the ^{31}P NMR parameters which are sensitive to the average properties of the electronic structure (Knight shift and spin-lattice relaxation time) do not differ for amorphous Ni-P alloys prepared by different techniques whereas the fluctuations in the electronic structure as seen by the field-dependent linewidth parameter k_1 are higher in alloys obtained by chemical reduction from chloridic bath than in the case of the other three preparation methods.

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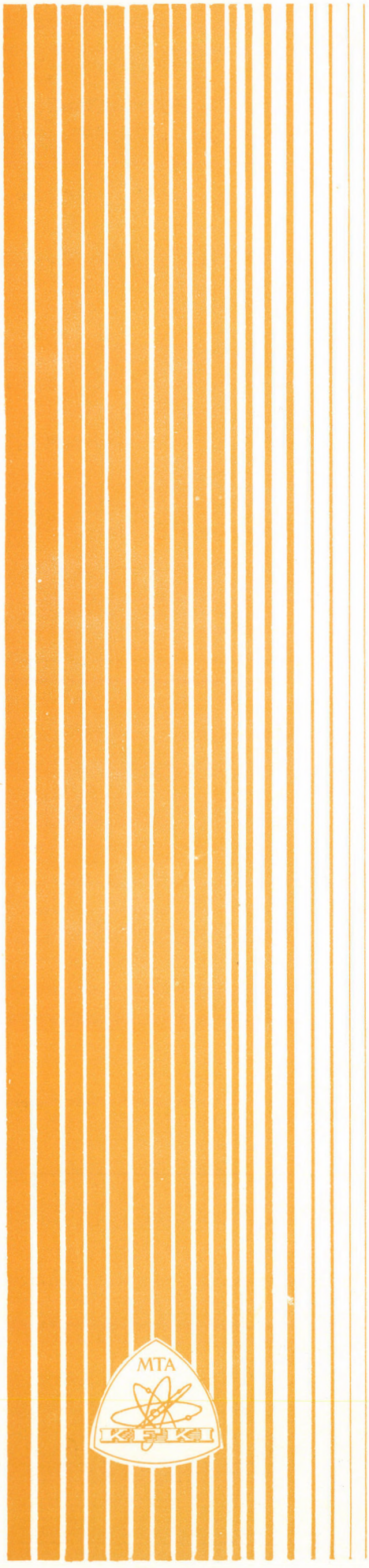

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